

Supporting Information for Acceptor-Donor-Acceptor small molecules based on derivatives of 3,4-ethylenedioxythiophene for solution processed organic solar cells.

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General Remarks

Reagents were purchased and used as received unless stated otherwise. Apart from chloroform which was distilled over calcium hydride before use, all other dry solvents were obtained from a solvent purification system (SPS 400 from Innovative Technologies) that used alumina as a drying agent. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE III 400 instrument at 400 and 101 MHz respectively. Chemical shifts are given in ppm; all *J* values are in Hz. Elemental analyses were carried out on a Perkin-Elmer 2400 analyser. High resolution mass spectrometry (HRMS) was performed by the EPSRC national facility at Swansea. Melting points were determined using a TA Instrument DSC Q1000 Differential Scanning Calorimeter and are uncorrected. Thermal gravimetric analysis (TGA) was performed on a Perkin Elmer thermogravimetric analyser TGA 7 at a temperature profile of 40 - 550°C at 10°C min⁻¹ under argon. UV/vis measurements were carried out on a Shimadzu UV-2600 spectrometer, on small molecule solutions (10⁻⁵ M) in chloroform. Cyclic voltammetry was carried out on a C-H instrument electrochemical workstation CH1660E on solutions of the three A-D-A small molecules (10⁻⁴ M in anhydrous dichloromethane) with tetrabutylammonium hexafluorophosphate as the supporting electrolyte (0.1 M). The data obtained were referenced to the *E*_{1/2} of ferrocene/ferrocenium (Fc/Fc⁺) redox couple taking

the HOMO of ferrocene to be -4.80 eV. Glassy carbon, platinum wire and silver wire were used as working, counter and quasi-reference electrodes, respectively.

Organic photovoltaic (OPV) devices were fabricated using blended chloroform solutions of A-D-A small molecule donor (10 mg ml⁻¹) and PC₇₁BM acceptor (10, 20, 30 or 40 mg ml⁻¹) and stirred overnight at 40°C. Patterned indium doped tin oxide (ITO)/glass substrates were washed using deionised water, acetone and propan-2-ol under ultrasonication for 20 minutes in each solvent before being dried over a stream of compressed air. The substrates were then cleaned with UV ozone treatment for 2 minutes. PEDOT:PSS (Clevios P VP Al 4083) was then deposited onto the ITO substrates at a spin speed of 2000 rpm and annealed at 120°C for 20 minutes. The donor/PC₇₁BM blend solution was spin-coated on top of the PEDOT:PSS layer and annealed at various temperatures for 20 minutes before being transferred to the evaporation chamber. A 40 nm thick calcium layer followed by a 40 nm aluminium layer were thermally evaporated at a pressure of 6×10^{-6} mbar as top electrodes. The geometry of the electrodes was defined by a shadow mask giving the electrodes deposited a 6 mm² area. Current–voltage characteristics were measured using a Keithley 4200. Solar cells were illuminated by a Newport Solar Simulator with a calibrated standard solar cell. Active material deposition, electrode deposition and characterisation procedures were performed in an oxygen-free environment using a nitrogen-filled glove box (MBraun). Device performance was calculated from an average of three devices.

Synthesis

5-Bromo-4-hexylthiophene-2-carbaldehyde was prepared from 3-bromothiophene in three steps according to the literature.¹⁷ C-H activation was employed in the di-coupling of 5-bromo-4-hexylthiophene-2-carbaldehyde to EDOT yielding **2TE** precursor. A-D-A small

molecules were synthesised *via* the Knoevenagel condensation of **2TE** and acceptors (1,3-indanedione, 3-ethylrhodanine and ethyl cyanoacetate) as outlined below.

Experimental

2TE: 5-Bromo-4-hexylthiophene-2-carbaldehyde (9.85 g, 35.8 mmol), 2,3-dihydrothieno[3,4-b][1,4]dioxine (1.74 ml, 16.27 mmol), pivalic acid (0.997 g, 9.76 mmol) and caesium carbonate (15.90 g, 48.8 mmol) were dissolved in dry DMF (50 ml) and degassed with nitrogen for 30 mins. Palladium (II) acetate (0.146 g, 1.301 mmol) and tricyclohexylphosphonium tetrafluoroborate (0.479 g, 0.651 mmol) were added and the reaction stirred at 110°C for 16 hrs. The reaction mixture was then cooled to room temperature, quenched with 2M HCl (5 ml) and extracted into dichloromethane (70 ml). The organic extracts were combined, washed with deionised water (100 ml), dried over MgSO₄ and the solvents removed under vacuum. The compound was purified by column chromatography on silica gel (hexane:ethyl acetate / 7:3), dissolved in dichloromethane (70 ml) and precipitated by addition of hexane (140 ml) to give **2TE** (6.00 g, 70%) as an orange powder (mp 45-47 °C). ¹H NMR (400 MHz, CDCl₃) δ 9.86 (s, 2H), 7.59 (s, 2H), 4.42 (s, 4H), 3.00 – 2.69 (m, 4H), 1.75 – 1.63 (m, 4H), 1.41 (m, 4H), 1.32 (m, 8H), 0.89 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 182.2, 140.6, 138.9, 137.7, 137.0, 110.4, 64.3, 31.1, 29.7, 29.4, 28.7, 22.0, 13.5 (one carbon missing). MALDI-MS: *m/z* 530.26 [M⁺].

DIN-2TE: Compound **2TE** (0.200 g, 0.376 mmol) and 1,3-indanedione (0.550 g, 3.768 mmol) were dissolved in dry chloroform (50 ml). Triethylamine (0.2 ml) was added and the mixture refluxed with stirring under nitrogen for 16 hrs. The reaction mixture was cooled to room temperature and the solvents removed under vacuum. The crude product was dissolved in

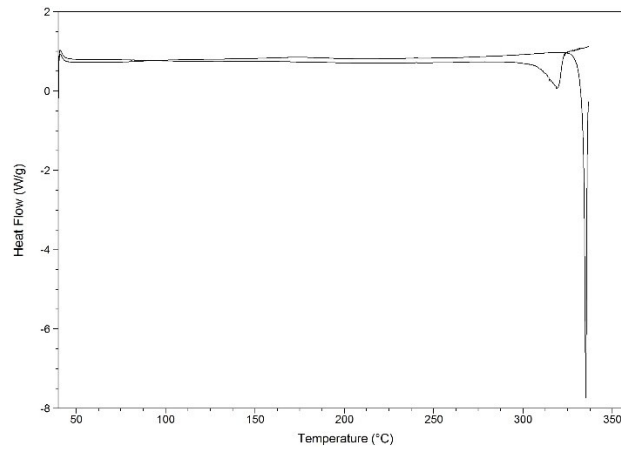
chloroform (50 ml), precipitated with methanol (100 ml) and purified by column chromatography on silica gel (chloroform) followed by repeated precipitation from chloroform with methanol to afford **DIN-2TE** (0.195 g, 66%) as a deep-blue solid (mp above 300°C). ¹H NMR (400 MHz, CDCl₃) δ 7.98 (m, 6H), 7.91 (s, 2H), 7.77 (m, 4H), 4.53 (s, 4H), 2.92 (m, 4H), 1.77 (m, 4H), 1.37 (m, 12H), 0.92 (t, *J* = 6.4 Hz, 6H); ¹³C NMR data not obtained due to poor solubility; HRMS (ASAP⁺, *m/z*) calc. for C₄₆H₄₂O₆S₃: 787.2222 [M+H]⁺, found 787.2215; *T_M* 335°C

DRH-2TE: Compound **2TE** (0.30 g, 0.565 mmol) was dissolved in dry chloroform (50 ml). Piperidine (0.11 ml, 0.753 mmol) and 3-ethylrhodanine (0.91 g, 5.56 mmol) were then added and the reaction mixture refluxed with stirring under nitrogen for 16 hrs. The reaction mixture was cooled to room temperature and extracted into dichloromethane (70 ml). The combined extracts were washed with deionised water (100 ml), dried over MgSO₄ and the solvents removed under vacuum. The crude product was dissolved in chloroform (50 ml), precipitated with methanol (100 ml) and then further purified by column chromatography on silica gel (chloroform: hexane / 2:3) followed by repeated precipitation from chloroform with methanol to afford **DRH-2TE** (0.247 g, 54%) as a dark reddish-brown solid (mp 250-252°C). ¹H NMR (400 MHz, CDCl₃) δ 7.81 (s, 2H), 7.23 (s, 2H), 4.48 (s, 4H), 4.19 (q, *J* = 7.1 Hz, 4H), 2.84 (m, 4H), 1.69 (m, 4H), 1.41 (m, 4H), 1.32 (m, 14H), 0.89 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 191.9, 166.8, 141.3, 138.6, 136.2, 135.8, 124.8, 119.6, 110.6, 64.5, 39.4, 31.2, 29.8, 29.4, 28.8, 22.1, 13.6, 11.8. HRMS (ASAP⁺, *m/z*) calc. for C₃₈H₄₅N₂O₄S₇: 817.1424 [M+H]⁺, found 817.1418. Anal. Calc. for C₃₈H₄₄N₂O₄S₇: C, 55.85; H, 5.45; N, 3.43. Found: C, 55.76; H, 5.43; N, 3.29. *T_M* 249°C.

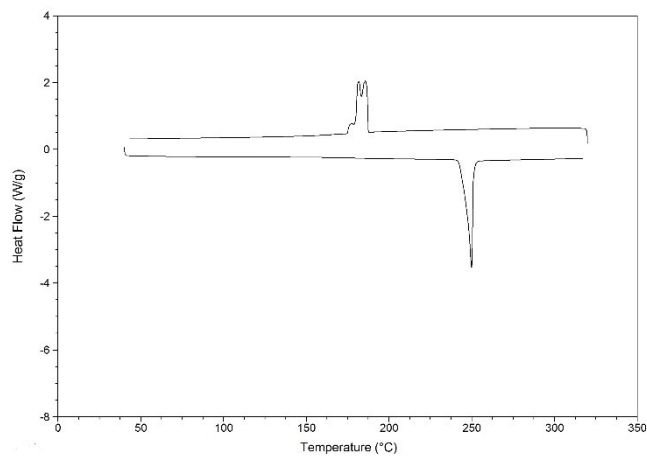
DECA-2TE: Compound **2TE** (0.21 g, 0.39 mmol) was dissolved in a mixture of dry chloroform (50 ml) and triethylamine (0.11 ml, 0.753 mmol). Ethyl cyanoacetate (0.96 ml, 9.10 mmol) was added and the reaction mixture refluxed under nitrogen for 18 hrs. The reaction mixture was then cooled to room temperature and extracted into dichloromethane (3 × 30 ml). The combined organic extracts were washed with deionised water (100 ml), dried over MgSO₄ and the solvents were removed under vacuum. The crude material was dissolved in chloroform (50 ml), precipitated with methanol (100 ml) then purified by column chromatography on silica gel (dichloromethane:hexane / 5:1). Further purification was achieved by repeated precipitation from chloroform (60 ml) with methanol (120 ml) to afford **DECA-2TE** (0.156 g, 55%) as a deep brown solid (mp 237-239°C). ¹H NMR (400 MHz, CDCl₃) δ 8.21 (s, 2H), 7.65 (s, 2H), 4.45 (s, 4H), 4.36 (q, *J* = 7.1 Hz, 4H), 2.84 (m, 4H), 1.69 (m, 4H), 1.41 (m, 10H), 1.32 (m, 8H), 0.89 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 163.4, 146.2, 141.8, 139.9, 139.7, 138.4, 134.3, 116.4, 111.6, 97.6, 65.2, 62.6, 31.9, 30.4, 30.1, 29.5, 22.8, 14.5, 14.3. HRMS (ASAP⁺, *m/z*) calc. for C₃₈H₄₅N₂O₆S₃: 721.2444 [M+H]⁺, found 722.2469. Anal. Calc. for C₃₈H₄₄N₂O₆S₃: C, 63.31; H, 6.15; N, 3.89. Found: C, 63.04; H, 6.09; N, 3.85. T_M 236°C.

DCS plots

a)



b)



c)

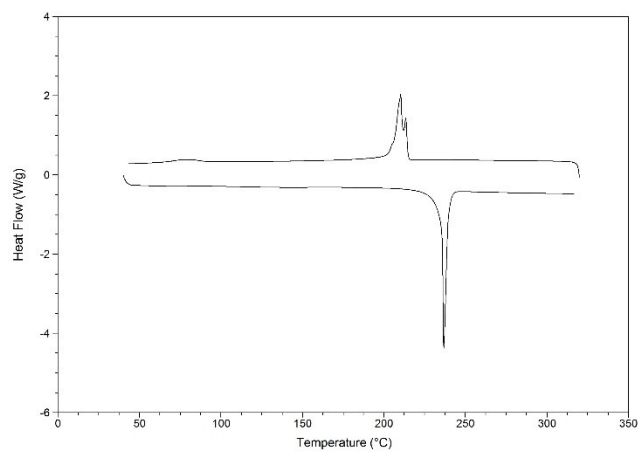


Figure SI-1: DSC plots of a) DIN-2TE b) DRH-2TE and c) DECA-2TE

Photovoltaic performance of fabricated devices.

Table SI-1: Photovoltaic performance of **DECA-2TE:PC₇₁BM** and **DRH-2TE:PC₇₁BM** devices at varied annealing temperature and donor/acceptor weight ratios.

Annealing temperature (°C)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)
DECA-2TE:PC₇₁BM				
1:1				
60	1.54	0.03	0.25	0.01
90	1.48	0.45	0.29	0.19
120	1.40	0.02	0.19	0.00
1:2				
60	1.80	0.87	0.38	0.60
90	1.62	0.86	0.37	0.52
120	1.44	0.88	0.37	0.48
1:3				
60	1.69	0.09	0.25	0.04
90	1.38	0.42	0.31	0.18
120	1.23	0.45	0.29	0.16
1:4				
60	2.96	0.85	0.41	1.03
90	2.71	0.84	0.36	0.84
120	2.88	0.82	0.37	0.88
DRH-2TE:PC₇₁BM				
1:1				
60	4.83	0.06	0.24	0.07
90	1.09	0.01	-0.07	0.02
120	1.32	0.36	0.29	0.14
1:2				
60	0.02	0.06	0.24	0.38
90	0.52	0.28	0.28	0.04
120	1.06	0.13	0.25	0.03
1:3				
60	1.49	0.67	0.31	0.32
90	3.21	0.64	0.30	0.63
120	1.19	0.68	0.30	0.24
1:4				
60	0.37	0.16	0.27	0.01
90	0.39	0.02	0.23	0.00
120	0.18	0.54	0.21	0.02

Table SI-2: Photovoltaic performance of **DECA-2TE:PC₇₁BM** and **DRH-2TE:PC₇₁BM** devices with varied diiodooctane (DIO) volume ratios.

DIO content (%)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)
DECA-2TE:PC₇₁BM_ 1:4 _60°C				
0.2	2.58	0.90	0.38	0.89
0.5	3.02	0.88	0.34	0.93
1	2.99	0.90	0.39	1.05
2	1.28	0.90	0.36	0.42
DRH-2TE:PC₇₁BM_ 1:3 _90°C				
0.2	4.23	0.83	0.32	1.15
0.5	4.64	0.85	0.30	1.20
1	5.60	0.68	0.35	1.36
2	1.79	0.44	0.29	0.23